

## A METHOD OF FABRICATING POLYCRYSTALLINE SILICON PLATES

The present invention relates to a method of fabricating polycrystalline silicon plates, in particular plates of small thickness, with at least one of the two  
5 faces of each plate having predetermined relief. The relief may be present over the major portion of the face (as occurs with texturing, for example) and/or over a small portion (as occurs with marking a plate or when reinforcing its stiffness by ribs). The method applies  
10 most particularly to fabricating solar cells, also known as photovoltaic cells or solarcells.

A typical photovoltaic cell is a diode with an n-p junction, the junction being very shallow and parallel to the surface. When illuminated, photons of energy  $h\nu$   
15 greater than the forbidden bandwidth  $E_g$  of the semiconductor are absorbed and create electron-hole pairs. The minority carriers as generated in this way (holes in the n zone and electrons in the p zone) are collected by the n-p junction. This results in a current  
20  $I_{ph}$ , that flows from the n region towards the p region. Metal contacts are made on the surface of the n-type zone (emitter) and on the rear face of the p-type zone (base) in order to collect the current.

The market for photovoltaic electricity is dominated  
25 by photovoltaic cells of the n-p (or p-n) junction type made on crystallized silicon. It is always necessary to seek a maximum value for the density of the photocurrent generated under given illumination. This amounts to maximizing collection of minority carriers generated by  
30 the useful fraction of the incident radiation (photons of energy  $h\nu > E_g$ ). Several techniques are used for this purpose. By way of example, mention can be made of: increasing the thickness of the base in order to enable long-wavelength photons close to infrared to be absorbed  
35 (but to the detriment of silicon consumption); reducing the depth of the junction in order to encourage the absorption, in the base, of short-wavelength photons,

close to UV; depositing an anti-reflection layer on the illuminated face in order to improve collection of incident radiation; or indeed reducing recombination processes at the interfaces (front face, rear face, contacts).

A final technique is texturing the surface. This technique, e.g. described in the article by J. Nijs, J. Szlufcik, J. Poortmans et al., published in IEEE Trans. Electron Devices 46 (10) (1999) 1948, consists in forming surface relief, in other words in texturing the surface so as to form pyramids. Figure 1 shows the principle on which this technique operates. The face of the silicon layer 12 that receives light is made up of an array of quasi-identical and adjacent pyramids 14 (represented by triangles in section) having side faces forming an angle of about  $45^\circ$  relative to the bases of the pyramids. An incident light beam 16 normal to the surface gives rise firstly to a refracted beam 18 which is absorbed in the layer 12, and secondly to a reflected beam 20. The reflected beam strikes the adjacent pyramid and gives rise firstly to a reflected beam 22 going away from the silicon layer and is therefore lost, and secondly to a first refracted beam 24 followed by a second refracted beam 26 that is absorbed by the layer. The relief thus increases the overall efficiency of the photovoltaic cell. Specifically:

- the effective coefficient of reflection for light on the entry face is reduced, in particular when the incident light presents a large component of diffuse light; and
- the angle of inclination of light rays that propagate in the base relative to the macroscopic surface of the photovoltaic cell is greatly increased, which has two consequences: firstly there is an increase in propagation distance within the base of the semiconductor; and secondly there is an increase in the coefficient of reflection of light on the rear face of

the semiconductor. These two effects increase the probability of long-wavelength photons being absorbed. Consequently, they contribute to increasing the density of the photocurrent and the open-circuit voltage of the solarcell compared with a solarcell in which the silicon layer has faces that are plane.

The presence of such texturing becomes very important for maintaining high conversion efficiencies when it is desired to reduce drastically the thickness of the silicon layer typically from around 300 micrometers ( $\mu\text{m}$ ) or 350  $\mu\text{m}$  (conventional photovoltaic cells), down to less than 100  $\mu\text{m}$ , or down to 50  $\mu\text{m}$  (or even less), in order to reduce the cost of such devices. In this range, and while the coefficient of reflection on the rear face is typically less than 0.6 (normal incidence on the rear face), a large fraction of the spectrum of the incident radiation propagating close to the normal at the surface is not absorbed in the thickness of the material unless special precautions are taken.

One of the applications of the present invention lies in texturing polycrystalline silicon layers in order to fabricate solar cells, and it is particularly advantageous for layers of small thickness, less than 300  $\mu\text{m}$ . Texturing consists in imparting predetermined relief to the surface of the layer, for example an array of parallel grooves or an array of pyramids.

In a first known texturing technique, that applies only to single crystal silicon plates having their surface close to the (100) crystal plane, texturing is performing by chemically etching the surface using a solution of KOH and isopropanol. Such etching is highly anisotropic and specific to the (100) crystallographic face, and enables very regular pyramids of micrometer size that are inclined at  $45^\circ$  to be obtained on the macroscopic surface. However, that technique is much less effective when it is applied to plates of

polycrystalline silicon, as are being used more and more for reasons of cost.

Under such circumstances, other techniques have been tried. Nevertheless, those techniques rely on isotropic  
5 etching, i.e. etching that is assumed to attack all grains under similar conditions: chemical or electrochemical etching using an acid medium (described in the article by V.Y. Yerokhov, R. Hezel, M. Lipinski, R. Ciach, H. Nagel, A. Mylyanych, P. Panek, Solar Energy  
10 Materials & Solar Cells 72 (2002) 291-298), reactive ion etching (RIE) in a gas, e.g. using a plasma containing chlorinated species (described in the article by S. Fujii, Y. Fukawa, H. Takahashi, Y. Inomata, K. Okada, K. Fukui, K. Shirasawa, Solar Energy Materials & Solar  
15 Cells 65 (2001) 269-275).

Another known technique relates to mechanical etching described in the article by F. Duerinckx, J. Szulfcik, J. Nijs, R. Mertens, C. Gerhards, C. Markmann, P. Fath, G. Willek, High efficiency,  
20 mechanically V.textured, screen printed multicrystalline silicon solar cells with silicon nitride passivation, Proceedings 2nd World Conference on PV Solar Energy Conversion, 1998. Mechanical etching consists in forming relief mechanically, e.g. an array of mutually parallel  
25 grooves or pyramids directly on the surface of the layer of silicon using mechanical tools such as a diamond grindwheel. Nevertheless, that operation considerably disturbs the structure of the silicon over a thickness of about 10  $\mu\text{m}$ , thereby having the effect of inducing  
30 defects throughout the volume of the silicon following the heat treatments to which the silicon is subjected subsequently. In addition, mechanical etching is slow and expensive and therefore industrially ineffective.

Each of those techniques presents limitations that  
35 are severe, either in terms of cost (electrochemical etching, plasma etching, and mechanical etching), or in terms of effectiveness (acid chemical etching). Several

of them are not applicable to plates that are very thin,  
of thickness smaller than 300  $\mu\text{m}$ , which are generally  
very fragile, given the manipulations and/or the  
mechanical stresses they involve. That applies to  
5 mechanical etching and to some extent to electrochemical  
cleaning (manipulations). The method of the present  
invention does not present the above drawbacks.

Another application of the present invention relates  
to marking plates in order to enable a plate or a series  
10 of silicon plates to be distinguished from other silicon  
plates.

Another application of the present invention lies in  
reinforcing the stiffness of thin silicon plates.

In general, the present invention solves the problem  
15 of embossing polycrystalline silicon plates, in  
particular of small thickness, less than 300  $\mu\text{m}$ , by  
proposing a method that is less expensive than prior art  
methods, and effective since it does not disturb the  
internal structure of the silicon, and since it can be  
20 implemented industrially.

More precisely, the invention provides a method of  
fabricating at least one polycrystalline silicon plate  
with one of its two faces presenting predetermined  
relief, in which method a layer of polycrystalline  
25 silicon is deposited on at least one of the two faces of  
a support, the method being characterized by the steps  
of:

- embossing said face of the support to impart  
thereto a shape that is complementary to said relief;
- 30 · depositing said polycrystalline silicon layer on  
said embossed face of the support, the surface of said  
polycrystalline silicon layer situated in contact with  
said embossed face then taking on the shape of said  
relief;
- 35 · cutting up said polycrystalline silicon layer; and  
· eliminating said support in order to obtain said  
polycrystalline silicon plate.

The predetermined relief may perform one or more functions. For example it may serve to texture the face(s) of the silicon plate. Under such circumstances, the relief occupies at least the major portion of the face(s). In addition to, or independently of, texturing, the relief may serve to mark the silicon layer with a reference for distinguishing the plate, or a series of plates derived from the silicon layer, relative to other silicon plates. When the relief involves only a portion of the plate, it may also serve to increase the stiffness of thin silicon plates, which are themselves relatively flexible, by creating ribs.

Since the invention applies most particularly to fabricating solar cells, said relief can be selected in such a manner as to texture the major portion of the surface of the silicon layer so as to increase the probability of incident light being absorbed in said layer.

In a first variant implementation of the invention, said texturing relief is in the form of an array of substantially identical pyramids, the side faces of each of said pyramids preferably forming angles substantially equal to  $45^\circ$  relative to the base of the pyramid. The height of such a pyramid advantageously lies in the range 1  $\mu\text{m}$  to 10  $\mu\text{m}$ .

In another variant implementation, said support is a carbon tape covered in a protective coating of pyrolytic graphite before its surface is embossed to impart said complementary-shape relief thereto.

Said face of the support may be embossed to give it a shape that is complementary to said relief by pressing a die against said support, the embossing surface of the die having the shape of a plane surface with said predetermined relief embossed thereon.

In another variant implementation of the invention, said face of the support is embossed to give it a shape complementary to said relief by pinching said support

between two rollers and running it through between them, with the embossing surface of at least one of said rollers presenting the shape of said predetermined relief.

5        Said embossing surface of said die or of said roller is preferably made of a material selected from: carbon, silicon carbide, silicon, and silicon nitride.

Advantageously, the embossing surfaces of both rollers have the shape of said relief, the two faces of  
10        said support then taking on the shape complementary to said relief on the support being pinched between and running through said rollers.

In another variant implementation, a polycrystalline silicon layer is deposited simultaneously and  
15        continuously on both faces of said tape by causing it to pass through a bath of molten silicon and by pulling it vertically upwards at constant speed so as to leave said bath, thereby obtaining two polycrystalline silicon layers, each having a surface with said relief.

20        Said support is preferably burnt off by heating the assembly constituted by the support and the polycrystalline silicon to a high temperature, and thereafter the face of the polycrystalline silicon having the shape of said relief is cleaned.

25        Advantageously, said support has thickness lying in the range 200  $\mu\text{m}$  to 350  $\mu\text{m}$ , preferably in the range 200  $\mu\text{m}$  to 300  $\mu\text{m}$ , the layer of polycrystalline silicon has thickness lying in the range 40  $\mu\text{m}$  to 300  $\mu\text{m}$ , and the thickness of said protective coating is substantially  
30        equal to 1  $\mu\text{m}$ .

In another variant implementation, said relief is composed, independently of or in addition to, texturing, by a pattern characterizing said plate or a series of plates of silicon. By way of example, the pattern may be  
35        a bar code or a reference number.

In another variant implementation, independently of, or in addition to, texturing and/or the pattern

characterizing the plate, notches are embossed in said face of said support so that ribs of shape complementary to the notches are formed on said surface of the silicon layer, thereby having the effect of increasing the  
5 stiffness of the silicon layer. The depth of said notches may be several tens of micrometers and the greatest width of said ribs may be a few millimeters at most.

In another variant implementation, each of said  
10 rollers is formed by at least two knurling wheels, each having a face forming an embossed face, the knurling wheels being separated by a disk having a portion projecting beyond the embossing faces of the wheels, the embossing surfaces of the rollers then being constituted  
15 by the embossing faces of the knurling wheels forming the texturing and/or the pattern in the layer of silicon, plus the projecting portion of the disk forming the relief in the form of a rib perpendicular to the axis of rotation of said roller. Advantageously, each of the  
20 rollers is made up of a succession of knurling wheels separated by disks, each of the disks having a portion that projects beyond the surfaces of the knurling wheels, the spacing between said disks constituting the pattern that characterizes said plate or said series of plates of  
25 polycrystalline silicon.

In a another variant implementation, said rollers or said knurling wheels have longitudinal strips parallel to the axes of rotation of said rollers or knurling wheels. These longitudinal strips can coexist with the  
30 projections constituted by said disks.

Other advantages and characteristics of the invention appear in the following description of implementations given as non-limiting examples and described with reference to the accompanying drawings, in  
35 which:



· Figure 1 shows the path of an incident light beam in a layer of silicon whose front surface has been textured to give it relief in the form of pyramids;

· Figure 2 is a diagram showing the method of  
5 texturing both faces of the silicon layer support;

· Figure 3 shows the support and the silicon layers obtained at different steps of the method of fabricating textured silicon layers;

· Figure 4 is a diagram showing the preferred  
10 implementation of the method of fabricating textured layers;

· Figure 5 is a diagram showing rollers made up of knurling wheels and disks enabling the surface of the silicon layer to be textured and/or marked and ribbed by  
15 means of a step of embossing the support; and

· Figure 6 is a diagrammatic section view of a knurling wheel provided with longitudinal strips parallel to its axis of rotation.

In the method of the invention, one or more thin  
20 plates of polycrystalline silicon are fabricated mainly by depositing silicon in the form of a thin layer on one or both previously-embossed faces of a support. Since the silicon is deposited on the surface in relief of the support, the silicon matches the shape of the relief. In  
25 other words, the shape of the face of the layer of silicon that is in contact with the support is obtained by molding liquid silicon on the support. The relief of the face of the support is thus selected to be of a shape that is complementary to the shape that is to be given to  
30 the relief on the face of the thin layer.

Figures 2, 3, and 4 show the preferred embodiment of the invention in which two textured, marked, and/or ribbed layers of silicon are fabricated simultaneously by depositing the silicon on both faces of a support  
35 constituted by a tape. The first step of the method consists in giving both faces of the tape a shape that is complementary to the predetermined shape that is to be

obtained for the faces of the two layers of silicon, i.e. the faces facing the support. This is shown in Figure 2, where the tape 28 (shown in section) is pinched between two rollers 30 and 32. These rollers are cylindrical in shape and they revolve about their axes of rotation 34 and 36 respectively in the directions of arrows 38 and 40, thereby pulling the tape 28 upwards, in the direction of arrow 42. In another embodiment, the rollers 30 and 40 are mounted to turn freely about their axes of rotation 34 and 36, with the tape 28 being driven by other means independently of the rollers.

The embossing surfaces of these rollers, which are preferably made of carbon, silicon carbide, silicon, or silicon nitride, present the shape of the predetermined relief 44 that is to be given to the surface of the layer of silicon. The tape 28 is preferably made of carbon (laminated expanded graphite), a flexible material of small elasticity and low density (relative density lying in the range 0.6 to 1.3). By way of example, this carbon is as sold under the name "Papyex" by the supplier La Carbone Lorraine, "Sigraflex" by the supplier SGL Carbon, or "Grafoil" by the supplier Union Carbide. The relatively inelastic nature of these materials makes it possible to obtain an excellent molding of the relief 44 on the rollers on each of the surfaces 46 and 48 of the tape while the tape 28 is passing between the rollers 30 and 32. The approximate thickness of the tape 28 is 200  $\mu\text{m}$  to 300  $\mu\text{m}$  and it can be supplied in the form of rolls having a width of 1 meter (m) and a length of several hundreds of meters. Nevertheless, in the implementation described herein, it is preferable to use a width of about 15 centimeters (cm).

Figure 2 is merely a diagrammatic view and represents relief 44 that may be in the form of an array of grooves that are parallel or perpendicular relative to the axes of rotation 34 and 36 of the rollers, when the objective is to texture the faces of the silicon layers.

In the first configuration, the grooves are horizontal and extend across the width of the tape. In the second configuration, the grooves are vertical and extend lengthwise relative to the tape. In both configurations, an anisotropic array is obtained having one dimension. It should be observed that these two patterns applied to texturing the support tape give the same result from the point of view of texturing the silicon plate, as would be obtained by texturing the silicon directly in mechanical manner with a diamond, but without the drawbacks of that technique (slow, aggressive, and requiring finishing by deep chemical etching to eliminate the damage done by diamond etching). Preferably, the relief 44 may also be an array of adjacent pyramids as shown in Figure 1. Whenever the application is for texturing the surface, the shape of the relief is selected so as to increase the probability of incident light being absorbed in the silicon layer.

Figure 3 shows the following steps in fabricating silicon layers. In Figure 3A, there can be seen a carbon tape 50 with both of its faces 52 and 54 being textured by implementing the technique shown in Figure 2. These two faces 52 and 54 are then covered (Figure 3B) in a fine protective layer 56, 58 of pyrolytic graphite or pyrolytic carbon of micrometer thickness. Because of the very small thickness of this layer, the relief of the faces 52 and 54 is conserved. This protective coating is necessary because the carbon of the tape 50 reacts with molten silicon to give rise to silicon carbide, while pyrolytic graphite is inert relative to molten silicon.

Figure 3C shows the resulting carbon tape of Figure 3B with its faces in relief 56 and 58 having the two layers 60 and 62 of polycrystalline silicon deposited thereon. The preferred technique for depositing these layers is shown in Figure 4. The tape serves simultaneously as a support for the silicon layers and as means for texturing, marking, and/or ribbing the faces 64

and 66 of the silicon layers that face the tape, thereby imparting the predetermined relief 44 of the rollers 30 and 32 (Figure 2). The faces 64 and 66 of the silicon layers take on the shape of the respective embossed faces 56 and 58 as in a molding technique. This relief is complementary in shape to the shape of the faces 56 and 58 of the support tape 50; it is therefore identical to shape to the relief 44 on the rollers 30 and 32 of Figure 2. The layers of silicon are thus given the desired predetermined shape in relief.

The following step consists initially in cutting up the composite tape made of the tape 50 plus the silicon layers 60 and 62 into plates, generally of rectangular shape. Then the support tape 50 is eliminated (Figure 3D) by being burnt off in air at high temperature (about 1000°C) in order to obtain two plates 68 and 70 of polycrystalline silicon. Thereafter, the textured faces of the plates are subjected to light cleaning in order to eliminate the oxidized layers of silica that form on their surfaces. These oxidized layers are of very small thickness, of the order of a few tenths of a micrometer. Cleaning can be performed using various conventional techniques, e.g. using gaseous hydrofluoric acid, a 5% aqueous solution of hydrofluoric acid in water, possibly having 10% nitric acid added to, or indeed by reactive ion etching (RIE) in a gas, e.g. by means of a plasma containing chlorinated species.

The silicon layers 60 and 62 are advantageously deposited on the support tape 50 using the method shown in Figure 4. This method, referred to as the silicon tape on temporary carbon substrate (TTS) method, is described in several patents, for example: FR 2 386 359, FR 2 550 965, or FR 2 568 490. Nevertheless, the method described in those patents does not make use of an embossed carbon tape for the tape 50. The layers of silicon fabricated in accordance with the teaching of those patents are therefore not embossed (e.g. textured,

marked, and/or ribbed). In Figure 4, the faces 74 and 76 of a flexible carbon tape 72 (identical to the tape 50 in Figure 3) are embossed (Figure 3A) so as to take the shape that is complementary to the predetermined relief by performing the method shown in Figure 2 and then being covered in a protective layer of pyrolytic graphite (Figure 3B). A silica or carbon crucible 78 contains a bath 80 of molten silicon together with means (not shown) for heating the silicon, e.g. heater resistance surrounding the crucible. The bottom of the crucible 78 includes a rectilinear slot 82 through which the carbon tape 72 passes vertically. The tape is set into vertical upward movement by means that are not shown, and it leaves the bath 80 by passing through its horizontal equilibrium surface 84. The width and the length of the slot 82 are determined so that the liquid silicon meniscus in this slot from a connection that is stable.

When the tape 72 moves in the direction of arrow 86, a polycrystalline silicon layer 88 or 90 is deposited on the respective embossed faces 74 and 76 of the support tape 72. This produces the equivalent of the carbon tape 50 and the layers 60 and 62 of Figure 3C. The assembly comprising the support tape plus the silicon layers is then cut up to form plates. Thereafter, the support tape 72 is eliminated and the two resulting layers of polycrystalline silicon are treated as described above with reference to Figure 3D.

The method described with reference to Figure 2 is implemented using two rollers 30 and 32 whose embossing surfaces carry relief in the form of pyramids, enabling the silicon layer to be textured. Figure 5 is a diagram showing an embodiment of rollers suitable for texturing and/or marking and ribbing the layer of silicon. Two facing rollers 92 and 94 revolve about respective parallel axes of rotation 96 and 98. A carbon tape 100 (shown in section perpendicularly to its length) that is to act as a support for the layers of polycrystalline

silicon is pinched between the rollers 92 and 94 and travels between the rollers in a direction perpendicular to the sheet of the drawing. The roller 92 is made up of a series of knurling wheels 102, 104, 106, and 108 that  
5 are separated by disks 110, 112, 114, and 116. These knurling wheels and disks have a common axis of rotation 96. Similarly, the roller 94 is made up of knurling wheels 118, 120, 122, and 124 separated by disks 126, 128, 130, and 132, the knurling wheels and disks having  
10 the axis 98 as their axis of rotation. The cylindrical surface (embossing surface) of each of the knurling wheels may have an embossing pattern or relief suitable for texturing and/or marking a reference on the carbon tape 100. The disks are of a diameter that is slightly  
15 greater than the diameter of the knurling wheels such that a portion 134 of each disk (its outer circumference) projects from the embossing surfaces of the knurling wheels. As a result, the relief embossed in the tape 100 by the disks 110 to 116 and 126 to 132 is in the form of  
20 grooves 136. By depositing the layer of silicon on the tape, e.g. using the method shown in Figure 4, the surface of the layer of silicon will include ribs of shape complementary to the grooves 136 and extending longitudinally relative to the tape 100. These ribs  
25 reinforce the stiffness of the silicon layer.

Grooves can also be formed across the width of the tape. To do this, the knurling wheels carry relief in the form of ribs located on their embossing surfaces. This is shown diagrammatically in Figure 6 where the  
30 knurling wheel 102 is shown in section perpendicularly to its axis of rotation 96. Ribs 138 are placed on the cylindrical embossing surface of this knurling wheel parallel to the axis of rotation 96. These ribs form grooves of complementary shape in the support tape 100  
35 and thus ribs of the same shape on the layer of silicon. Such ribs 138 can be located in the same manner on the embossing surfaces of all the other knurling wheels, or

on a fraction only thereof, depending on the relief that is desired on the silicon layer. The number and spacing of the ribs 138 can be varied.

By combining the disks of Figure 5 with the ribs of Figure 6, relief is obtained that is waffle-shaped, being constituted by a grid of ribs, some being in the length direction of the tape and the others being in the width direction. Under such circumstances, it is preferable for the ribs not to come directly into contact with the disks, but to be spaced apart therefrom by gaps of the order of 1 millimeter (mm) or less.

The greatest width of the ribs is preferably no more than 1 mm and their height is preferably a few tens of micrometers.

The section of the ribs may be of any shape that is appropriate for the intended purpose (e.g. reinforcing the stiffness of the silicon layer), e.g. they can be U-shaped or V-shaped.

The method of the invention provides an industrial solution to embossing polycrystalline silicon plates, such as texturing them, marking them, and/or reinforcing their stiffness, without there being any mechanical or chemical stress being applied to the plate. The internal structure of the silicon is therefore not damaged. When the predetermined relief is in the form of an array of substantially identical pyramid, the resulting texturing is completely isotropic and it is possible to modulate the period of the array of pyramids and the shape of the pyramid. The method can be implemented at low cost, the greatest cost involved lying in fabricating the rollers 30 and 32 or 92 and 94, which can be used in fabricating very many plates. The texturing that is obtained can be considerable (high density and/or intensity of the relief) thus enabling photovoltaic cells to be fabricated that present very good efficiency in converting light into electron-hole pairs. In addition, consumption of chemicals is very small, since chemicals are used only

for eliminating the layer of silica that forms while eliminating the carbon support tape by heating it.

In the preferred implementation of the invention described above, both faces of the carbon support tape  
5 are textured and two textured layers of polycrystalline silicon are fabricated simultaneously. Naturally, it is possible to texture only one face of the support tape (by texturing only one of the two rollers 30 and 32), thereby obtaining only one textured silicon layer, without that  
10 going beyond the ambit of the present invention. Similarly, a method other than that shown in Figure 4 could be used for depositing a layer of silicon on a support. Instead of using rollers for embossing the support tape, it is possible to use a die having a plane  
15 surface that is embossed with the predetermined relief.